US-PAT-NO: 6537459

DOCUMENT-IDENTIFIER: US 6537459 B1

TITLE: Method and apparatus for etching-manufacture of cylindrical elements

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Brief Summary Text - BSTX (30):
WO 97/42910 relates to a novel apertured flexible tubular member with an encasing for insertion into vessels of the body as part of a medical device.
For example, the invention can be used as catheters, including guide catheters and balloon catheters, guidewires, catheter sheaths for use with catheter introducers, or drug infusion catheter/guidewires. These catheters also relate to novel apertured flexible tubular stents which may be coated, for insertion into vessels, tracts or ducts. One embodiment is coated with a low friction material such as a low friction **polymer** so as to provide for lubricity.
Samples of materials that might be used are polyurethane, hydrogels, polyethylene, polytetrafluoroethylene (PTFE) and, in particular, one such material which might be used is TEFLON.RTM..

Detailed Description Text - DETX (16):
Photoresist materials may be selected from amongst the broad classes of photoresists which are known in the art and are commercially available. The systems may be positive-acting (becoming more soluble where irradiated or heated) or negative-acting (becoming less soluble where irradiated or heated).
The systems may be based upon polymerization or **polymer**

cleavage or upon
generation of more or less soluble species within a carrier medium (as with
diazo oxides or naphthoquinones in epoxy or other **polymer** systems). The
polymer systems useful may include a very wide variety of classes, including,
but not limited to polyacrylates (including poly(meth)acrylates), polyvinyl
resins, polyurethanes, epoxy resins, silane chemistry (polysilanes,
polysiloxanes, etc.), phenol/formaldehyde resins (both novolaks and resols),
and the like. Polymerizable systems having multiple classes of functionalities
(epoxy-silanes, (meth)acrylate silanes, aminosilanes, etc.) are also generally
useful. Initiator systems of many various types may also be used, such as
radiation-sensitive iodonium, sulfonium, diazonium and phosphonium salts,
triazine, s-triazines, biimidazoles, benzophenones, radiation-sensitive free
radical photoinitiators generally, radiation-sensitive cationic initiators
generally, radiation-sensitive acid generators, and the like. It is especially
desirable that the substantive photoresist remaining on the cylindrical metal
element after imaging and development exhibits some strong resistance to the
metal etchant solution used later in the process. If the photoresist does not
exhibit such strength, it may be too rapidly removed during the etching and
expose metal to the etchant in undesired areas.

Detailed Description Text - DETX (40):

It is preferred that this contact be an active contact, that is a contact
with some kinetic activity as by stirring a solution in which the element has
been placed, swishing the element through a solution, spraying the solution
against the surface, or the like); an optional scumming (scum removal)
treatment with optical powder, pumice scrub, or the like to

mildly remove or
abrade away scumming to make the surface to be chemically etched more uniform
in properties can be performed about here in the sequence of steps. It is to
be noted that the removal of residual resist material within the finely
developed image areas by the use of particulate materials in a slurry (e.g.,
particles having an average particle diameter of less than 25 microns or less
than 20 microns, preferably an average particle diameter of less than 10
microns with a particle size variation of less than 25 number percent of the
particles having a **deviation** above the average particle size of more than 30%
(and preferably no more than 25%). It is also preferred to use a very fine
slurry of particulates with average particles sizes less than 5, preferably
less than 3 and even less than 2 microns in average particle size diameter.
The particulate slurries are applied to the developed resist image with mild
agitation or pressure and then followed with a rinsing step (e.g., step 12,
following). This has been found to provide a sharper image, which is not
believed to have been disclosed within the photoresist imaging art for non-flat
(e.g., three dimensional or especially cylindrical) resist imaging.

Detailed Description Text - DETX (53):
The following information describes and circumscribes the best mode of
practicing the invention. I. In the selection of raw materials for **stents,** the
metal tubing is preferably a high quality, uniform composition and uniform
thickness metal tube. An example of the preferred metals are Nitinol or 316LSS
fully annealed stainless steel. The preferred range of dimensions for tubing
used in the present invention comprises: ID (Inside Diameter)=0.01 to 0.5 cm,

preferably about 0.051 inch (0.13 cm) Wall **thickness**
0.002-0.3 cm, preferably
0.0025-0.004 inches (0.0066-0.11 cm) OD (Outside
Diameter)=0.1 cm to 0.2 cm,
preferably 0.056 in.-0.059 in. (0.14-0.15 cm) Length=0.1 to
1.5 m, preferably
about 2 ft (0.61 m) Photoresist 1. Electrodeposited
Resist, Shipley Co.
Negative-acting photoresist, aqueous-based. 2. The
process is equally
amendable to the use of positive resist, such as Shipley
SP2029. II. Tube
Cutting Prior to Etching A. Tubing may be cut into shorter
(e.g., 6.25 inch,
15.9 cm) lengths using a rotating blade cutter III.
Pre-cleaning: A. Handling
Devices Used 1. Hand held screened basket to support
elements without
compressive damage B. Sprex.TM. Cleaner Dip Tank 1. Bath
Composition:
.about.1.5 wt % Sprex.TM.. A.C. powder Balance: city water;
Sprex is Du Boise
Sprex.TM. A.C. Cleaner, a caustic-based detergent 2.
Process settings:
Temp=145 to 180 degrees F., preferably about 166.degree.
F. Time=2-5 minutes
3. Parts are placed in a screened basket and dipped in the
tank for 2-5
minutes, then removed. C. DI Water Rinse 1. De-ionized
water spray, room
temperature, spray pressure of 5-8 psi, time=5-30 seconds,
preferably about 20
seconds 2. Tubes are hand-held in spray at various angles;
some spray is
directed into the interior of the tubes such that visible
flow can be seen
exiting the opposite end of the tube. D. HCl Acid Dip Tank
1. Bath
Composition: 25% HCl acid reagent, 36% HCl Balance city
water 2. Process
Settings: Temp=60-80 degrees F., preferably about
70.degree. F. Time=5-30
seconds, preferably about 20 seconds 3. Parts are
hand-held in tank E. DI
water rinse as per step C F. Dry Box 1. Process Settings:
Temp=115 to
145.degree. F., preferably 130.degree. F. Time=until dry,
generally 10-15

minutes 2. Parts are laid on absorbent sheets such as Kimwipes.TM., often air is blown through the interior halfway through the drying. Pressurized air nozzle, hand-held IV. Resist **Coating--currently** performed by electrophoretic deposition of resist **polymer** composition, A. Electro-deposited negative photoresist B. Performed in a tank C. Resist **thickness** at the end of the element is about 10 to 150 micrometers. VI. Resist Drying VII. Resist Imaging--This is described thoroughly above. A. Equipment 1. Laser source--pulsed laser, e.g., excimer laser 2. Optical focusing and focussing mirrors 3. Optical Aperture Mask--made by Buckbee-Mears St. Paul 4. Tube positioning fixture a. Silicon supporting element with a hole drilled into a face thereof which matches the OD of metal tube closely, and also has a piece taken out of the side where the laser is directed. 5. Motion Control Systems a. For tube: A motivating system, e.g., rotational assembly, attaches to one end of the support for the tube. The assembly directs the tube rotationally (turning about its longitudinal axis) and longitudinally, moving the supporting element parallel to the longitudinal axis. The system is preferably operated continuously (rotated and translated longitudinally) throughout imaging. b. For aperture mask: currently connects to S5 aperture mask (**thickness**=0.001 to 0.005 inches [0.025 to 0.076 mm], preferably about 0.002 in. [0.051 mm]) moves vertically on a screw system, but hydraulic, or electrically driven pulley, torque, or magnetic system may also be used. A wheel aperture mask which would rotate has also been investigated. It is to be noted that in its preferred operation, the aperture mask only moves periodically. c. A computer controls both motion systems (that for the tube and that for the aperture); and could

also control the laser shutter as well. VII. Resist Developing A. Spray developing, with the resist developer being sprayed against all cylinder surfaces of the tube. The spray may be directed from all areas around the supporting tube as it is carried through a spray chamber and/or the tube may be turned in a chamber with fixed spray heads. The resist developer may also be applied by pad wiping application, dip application with some agitation within or after removal from the dip tank, and the like. VIII. Post-developing Burn-In/Re-Exposure of Resist A. A variety of burn-in methods were experimented with; including no burn-in. B. Conditions Tried 1. Pizza oven: temp setting=610.degree. F., time=25-30 seconds 2. Lower Temperature, IR heating: temp setting=450.degree. F., speed setting tube taped to a clip and hung on conveyor through vertical IR banks 3. Higher Temperature IR oven: temp setting=1150.degree. F., speed setting=25-35 Tubes ran as above; note this is a different machine than the lower T IR 4. None (no burn-in) 5. Dry box; temp=150.degree. F., time=90 minutes, tubing hung in dry box taped to clips IX. Resist Repair and spotting A. This process is manually performed and is intended to be eliminated in the future. It is done to improve the quality of some of the developed prints. Not all samples were spotted. B. Spotting material is hydrocarbon based; applied with a paintbrush with tube under magnification, to repair and fill in any handling scratches, pin holes, or other defects. X. Etching A. Equipment 1. Rotary Spray Etches a. constructed of etch resistant materials (Titanium, PVC) b. oscillating spray nozzles c. rotating flat d. further rotation of tube e. city water hose rinse f. light table for visual inspection 2. Tube Handling Fixture a. PVC round

flat-modified b. Titanium support rod supporting the metal tube to be etched fits on both ends of the tube and must penetrate into the opening into the tube sufficiently to maintain support of the tube, e.g., .about.0.02 to 0.90 inches, preferably about 0.045" into holes drilled in 2 PVC support bars. The fit is loose enough to allow for turning of the tubular metal about the support rod, but without sufficient clearance to allow unrestricted flow of etchant between the rod and the supported metal tube. c. An etch resistant gear-like (PVC pinwheel) is attached (permanently) to the Titanium rod so that the natural motion of the etchant spray will cause the Ti rod to rotate as the pinwheel is turned. The metal tubes (e.g., the stainless steel tubes) fit somewhat snugly onto the Ti rod; but some clearance exists, which allows for slipping the tubes on and the etched pieces off with minimal damage. 3. Rough Inspection Equipment (for Etch Time determined) a. Light Table b. 40.times. microscope c. PVC piece, 3/4" **thick,** with channel drilled in the middle. This provides a support for the microscope so that when the flat is laid on the light the Ti rod and sample lie deep in a channel near the top surface of the PVC piece. Then one can hold the microscope steady, adjust it easier, and even rotate the tube more easily. B. Etch Process Set Points--these are the most commonly used parameters for this application 1. Temperature=115-130.degree. F. 2. Baume=48.degree.B, .+-.7% (preferably for difficult to etch metals, between 47.5 and 55 Baume', more preferably between 48 and 55 Baume'. 3. Spray Pressure=10-25 psi; front & back nozzles 4. Spray oscillation speed=60 (setting on dial), approximately 8 to 40 sweeps or cycles (up and down) of the nozzle per minute. 5. Flat rotation speed setting=60 (e.g., the approximately

1 meter flat moves at a top edge speed between 0.1 or 1 and 30 cm/sec through
the spray area, more preferably between 1 and 5 cm/sec.) 6. HCL Acid
level=<1% 7. Etch time=10-14 minutes, dependent upon tube wall **thickness,**
etch composition and parameters, and other issues. C. Pre-Etch Scumming 1.
This optimizes the uniformity of the exposed metal surface on the developed
prints. Performed with the tubes already placed on the titanium rods,
hand-done at present. 2. Scumming with Optical Powder--rubbed w/cotton 3.
Scumming with Lan-O-Sheen.TM.--rubbed w/cotton 4. Electrocleaning of metal
surface XII. Stripping and Cleaning A. Handling Fixtures 1. Thin Stainless
steel rods a. Individual etched pieces are removed from the carrier and handled
using a very small stainless steel (often referred to herein as "SS") rod,
which fits loosely enough inside the cylinders that fluid can flow freely on
the inside surface. The tubes are stripped, cleaned, and dried while on this
rod, then placed back into the carrier. b. Thus far the rods have been
hand-held, 1 rod at-a-time, and hung in the tanks with bulldog clips
individually as well. Fixtures containing multiple thin SS rods are easily
produced. B. Both compositions: Stripper=RD68 and 30% RD68 (ChemClean CULX.TM.
Cleaner) (15% by KOH by volume) balance city water C. Process Settings:
Temp=160-180.degree. F., preferably about 175.degree. F. Time=3-10 minutes,
preferably about 5 minutes D. DI Water Rinse 1. Similar to Process C; DI Spray
is directed such that the resist is blown off of the tube. E. Isopropyl
Alcohol Rinse

Detailed Description Text - DETX (59):
The flat 200 comprises a supporting element 202 of etchant resistant

material (e.g., a polymeric or composite substrate, such as polyvinyl chloride or polyolefin **polymer**). The supporting element 202 is a flat sheet of the **polymer,** cut in a generally round shape with a diameter of from 0.3 to 2.0 meters, preferably from 0.5 to 1.5 meters. There is an opening 204 in the central area of the sheet, the opening preferably having parallel sides (e.g., 206 and/or 208b) within the opening. L-bars 210 are aligned along the opposed parallel sides 206. The L-bars 210 have supports (not shown) far the support elements 212 for the cylindrical elements 214 (which may be as simple as holes (not shown) into which the ends 216 of the flexible support elements 212 may be inserted). The L-bars 210 may contain a sufficient number of opposed holes (not shown) to support the desired number (e.g., 2-3 0) of supported cylindrical elements 214 which have already had the photoresist coatings imaged, developed and otherwise prepared for the etch process. The individual support elements 212 should not overlap or be so close to each other as to prevent the ready flow of etchant between them (or be so positioned that one element might intercept sprayed etehant before its straight-line path would cause it to contact another cylindrical element.